U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-260 253

STATUS REPORT - USE OF CHEMICALS AND OTHER MATERIALS TO TREAT OIL ON WATER

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
WASHINGTON, D. C.

24 FEBRUARY 1969

002301
253056

PB 260 253

CLEAN WATER

STATUS REPORT

USE OF CHEMICALS AND OTHER MATERIALS TO TREAT OIL ON WATER

NORTHEAST REGION RESEARCH & DEVELOPMENT PROGRAM
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
FEBRUARY 24, 1969

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

BIBLIOGRAPHIC DATA SHEET	1. Report No.	2.	3. Recipient's Accession No. PB-260 253
4. Title and Subtitle Status Report - Use of Chemicals and Other Materials to Treat Oil on Water			5. Report Date 24 Feb 69 6.
7. Author(s)			8. Performing Organization Rept. No.
9. Performing Organization Name and Address Federal Water Pollution Control Administration, Washington, D. C.			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Organization Name and Address			13. Type of Report & Period Covered 14.

15. Supplementary Notes

16. Abstracts

A statement by the research facilities of the Federal Water Pollution Control Administration on the use of various chemicals to treat oil on water is provided. Methods discussed include dispersal, absorption, sinking, gellation, and burning of oil from water surfaces and affected shorelines. Also included is the FWPCA policy on the use of chemicals to treat floating oil.

17. Key Words and Document Analysis. 17a. Descriptors

17b. Identifiers/Open-Ended Terms

*Water pollution control
Absorption
*Oil pollution removal
Dispersing
Chemical removal
Federal agencies

17c. COSATI Field/Group 13B

18. Availability Statement	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 25
	20. Security Class (This Page UNCLASSIFIED	22. Price $3.50 - 3.00

INTRODUCTION

The disastrous effects of significant oil spills into the water environment, together with remedial measures required, are described in "Oil Pollution - A Report to the President", submitted early in 1968. The use of chemical compounds has been considered to assist in the control of oil on the water and subsequent clean-up operation. Basically, chemicals are employed to disperse, gel, sink, absorb, and facilitate the burning of oil. The basis of present knowledge has resulted primarily from experience with the major spills involving the tankers TORREY CANYON and OCEAN EAGLE and with the offshore oil platform at Santa Barbara, California. In addition, the FWPCA is gaining valuable experience through giving technical assistance on actual spill incidents and is conducting broad research and development programs relating to the clean-up and control of oil in the water environment.

With the exception of gelling agents, chemicals have been used during the three major incidents, singly and in combination, with varying results. Each major incident differed to some extent with causes and immediate control of the sources of oil, the type and use of the water environment, and the nature and proximity of the shoreface. The resulting damage has primarily involved water-fowl fatalities, deposition of oil upon recreational beaches, and adverse effects to marine life.

C O N T E N T S

I. Introduction..... i

II. Summary..... 1

III. Sections

Dispersants..... 5

Floating Sorbents..... 11

Sinking Agents..... 15

Gelling Agents..... 18

Burning Agents..... 19

SUMMARY

This report provides a statement by the Research facilities of the FWPCA on the use of various chemicals to treat oil on water. Basically, these methods are employed to disperse, absorb, sink, gel, and facilitate burning of oil from the water surface and affected shorelines. Concerning use of chemicals, a number of factors must be carefully considered, most important of which are toxicity and overall effects upon the water environment, effectiveness of the methods utilized, and cost of obtaining and applying chemicals together with ensuing recovery and disposal operations.

Dispersants theoretically serve to increase the surface area of an oil slick and disperse oil globules throughout the larger volume of water thereby aiding in accelerated degradation of oils by microbiological means. Dispersants vary considerably in toxicity, effectiveness and ability to stabilize the oil after extended periods of time. Technology in properly applying dispersants over large oil slicks followed by necessary agitation is currently lacking. Use appears far more critical in harbor and estuary areas and in proximity to shore. Particular care in the use of these materials must be made where water supply might be affected. Desirability of employing dispersants in the open sea remains unsolved although this approach is potentially more promising pending additional field data. After widespread dispersant use, reports led to the conclusion that dispersants cause much more damage to aquatic life than oil alone. In the case of beaches, they actually compound the problem by adding to the amount of

pollutants present and by causing the oil to penetrate more deeply into the sand.

Floating Absorbents include a wide range of materials ideally with oil-attracting and water-repelling characteristics. Absorbents have unique advantages over other methods of oil cleanup but also a number of disadvantages including delivery and application of the material, and collection and disposal of the oil-absorbent mass. Straw is extensively used as an absorbent because of availability, cheapness and accepted effectiveness; large investment in equipment and manual labor is however implied. Natural products or those modified by heat and chemical treatment are currently used as absorbents. An additional group of absorbent products are those derived from the synthetic or plastic manufacturing field which hold potential promise; of these, polyurethane and polypropylene are in greatest use. Considerable agitation or interaction between the oil and the absorbent is highly desired. Absorbent application and their overall use become increasingly complex with the larger oil spills. The consequent problems of collection and disposal of the oily masses become enormous!

Sinking Agents when properly applied onto an oil slick adhere to the oil and there is subsequent absorption and sinking of the oily mass. Sinking absorbents should be evenly mixed with the slick and be given proper time reaction before the mass eventually sinks. There should also be little or no tendency for release of the oils back to the water environment. The

only large-scale use of sinkants was that made by the French following the TORREY CANYON. Opinion is still divided on the use of oil sinkants as to efficiency, cost, application, and possible environmental effects. It appears the utilization of sinking agents would be most advantageous in deeper ocean waters outside the heavier fishing zones and with minimum effects to productive biological life in the coastal zones.

Gelling Agents applied over the surface or periphery of an oil slick show promise as another approach for containing and cleaning up oil spills. Further development is advised for this class of chemicals.

Burning Agents offer an attractive and inexpensive means of disposing of large amounts of oil over the water surface. This course of action would seem inadvisable except in situations where the oil is sufficiently distant from the shoreline or other property subject to salvage. Past attempts to burn oil have been largely unsuccessful. However, because of the potential value of this method, further consideration should be given for improving and refining these procedures.

In considering the use of chemicals with oil spills, a number of factors must be carefully borne in mind. Of prime importance is the effect of the chemical or oil-chemical mixture on the water environment. The introduction of toxic chemicals in the water or on the shoreface can destroy the delicate balance of aquatic ecology and result in long-lasting damage or destruction of valuable species. The ability of the chemicals to accomplish the assigned task is a critical factor. The type of oil involved, the physical

and chemical nature of the water body, and the particular products used will relate to the effectiveness of the method. In major incidents involving spills of oil, the cost of obtaining and applying chemicals may range into millions of dollars.

DISPERSANTS

Scores of products are sold in this country for the purpose of emulsifying oils. Many have been developed for such uses as cleaning residual oil from cargo tanks before loading of fresh cargo. Of these, at least 70 have been claimed useful for dispersing oil from the surface of water. These products are known by a variety of names: emulsifiers, detergents, degreasers, dispersants, etc. For consistency, they will be referred to as dispersants since this term describes what they are intended to accomplish - the dispersion of oil into the large water body.

The primary components in most dispersants are surfactants, solvents, and stabilizers. Surfactants, by their affinity for both oil and water, alter the interaction between oil and water so the oil tends to spread and can be more easily dispersed into small globules - or what is commonly called an emulsion. Soap does the same thing to oil on our hands, allowing it to be emulsified or dispersed and washed away in water.

Solvents enable the active agent or surfactant, to mix with and penetrate into the oil slick and thusly form the emulsion. The solvent usually comprises the bulk of the dispersant product and may range from petroleum solvents such as kerosene to water solvents. Petroleum based solvents, chlorinated hydrocarbon solvents, if present, represent the most toxic component in the dispersant product but also dissipate rapidly in the water environment. Stabilizers which are the third major component in most dispersants, stabilize the emulsion once formed.

One theory behind the use of dispersants in oil pollution incidents is that they will provide a means of accelerating the rate of natural degradation of oil. We know that oil is degraded naturally at sea, although at a slow rate, which is probably limited by the surface area of the oil available to the microorganism populations. Increasing the surface area of the oil by dispersion is thought to accelerate this biological degradation.

Dispersants have been used for a number of years, for dispersing small oil slicks in several harbors in this country and abroad. Because of the small quantities involved, the environmental effects were minimal and the complaints limited. Few alternatives exist for handling oil spills and dispersants are easily obtained, transported and applied. They furthermore offer visible evidence of "doing something" about pollution incidents.

Their first major test came during the TORREY CANYON incident where 15,000 tons of dispersants were used to treat 75,000 tons of oil. Two-thirds of this amount was used for cleaning oil from contaminated shores and resulted in severe adverse effects on the aquatic life. The areas of the shore where dispersants were not used, but heavily polluted with oil alone, showed very minor damage according to J. E. Smith, Director of the Plymouth Laboratory of the Marine Biological Association of the United Kingdom, who studied the biological effects of the TORREY CANYON spill. These observations led to the conclusion that dispersants cause much more damage to aquatic life than oil alone.

The dispersants used during the TORREY CANYON incident were mostly solvent-based and highly toxic, killing marine organisms at concentrations around 10 parts per million.

The biological damage during the TORREY CANYON appeared to be limited to the shore areas. In the open sea where they were also used, there were no detectable effects on marine life. Officials from the United Kingdom took samples by trawling directly beneath slicks treated with emulsifiers and observed no deaths and no tainting of the flavor of commercial species. It must be noted that procedures for this type of sampling are not notably precise.

Current information indicates that dispersants vary considerably in toxicity. Various reports state that dispersants used during the TORREY CANYON incident were highly toxic. Since then, other less toxic dispersants are reported to have been developed. Fifty percent of marine killifish are killed within 24 hours by exposure to concentrations as low as 4 parts per million of one product, and as high as 10,000 parts per million of another.

Moreover, the combination of oil and dispersant may conceivably increase the toxicity of either the oil, the dispersant chemical, or both. The possibility of this "synergistic" action must be carefully examined. Dispersing the oil (which is toxic) may also aggravate the problem.

But toxicity is not the only consideration in the use of dispersants. Of equal significance is their effectiveness. Experience at San Juan, Puerto

Rico, and field tests conducted by research personnel at Edison, New Jersey, indicate that they are generally ineffective for cleaning oil from beach sand of the type found along our east coast. They actually compound the problem by adding to the amount of pollutants present and by causing the oil to penetrate more deeply into the sand. The "TORREY CANYON Pollution and Marine Life" report also noted that quicksand occurred as the result of using these materials.

Evaluation of the effectiveness of dispersants on water is much more difficult. It is hindered by the presence of natural dispersion and by a lack of adequate methods for measuring the amount of oil on water. Their effectiveness during the TORREY CANYON is still being debated. Subsequent incidents which are claimed to have demonstrated their effectiveness have been at remote locations and without impartial, qualified observers. In fairness to those involved in unfavorable reports, it should be mentioned that the methods of application of dispersants and of subsequent agitation, which are critical for effective performance, have not always been optimal.

The cost of dispersants ranges from two to four dollars per gallon. Using recommended doses, the cost of chemicals for dispersing a relatively small 500 barrel spill would be about $20,000. The cost for chemicals used on the TORREY CANYON oil exceeded $5 million. Adequate technology is lacking for their application. Slicks from large spills spread in micro-thin layers over hundreds of square miles. Efficient use of dispersants to

treat a complete slick would require proper density application and agitation of large areas of the sea surface. Such methods have not been developed.

Thus, the desirability of using dispersants on the open sea remains unresolved. The FWPCA is conducting research to help provide the answers. As an initial step an interim standard procedure has been developed for measuring the comparative acute toxicity of dispersants to selected aquatic organisms. This will allow the assessment of relative toxicity among equally effective dispersants. We are continuing to refine this procedure and refine our capability for predicting the effect of dispersants on the environment. Our research personnel are also developing a standard test for measuring the effectiveness of dispersants, so they may be rated on a common basis.

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

POLICY ON THE USE OF

CHEMICALS TO TREAT FLOATING OILS

1. Chemicals should not be used to emulsify, disperse, solubilize, or precipitate oil whenever the protection or preservation of (a) fresh water supply sources, (b) major shellfish or fin fish nurseries, harvesting grounds or passage areas, or (c) beaches is a prime concern.

   Such chemicals should only be used in those surface water areas and under those circumstances where preservation and protection of water related natural resources is judged not to be the highest priority or where a choice as to resource preservation may make the use of such materials a necessary alternative.

2. Examples of areas and circumstances where the use of such chemicals might be acceptable are:

   a. where fire or safety hazards are presented by the spill of a petroleum product;

   b. where large numbers of waterfowl may perish because of the proximity of floating oil;

   c. under certain conditions, as a "polishing" or final clean-up of light slicks of oil following mechanical removal of floating oils.

3. Chemicals that emulsify, disperse, solubilize or precipitate oil should be used only under the immediate supervision of the Federal Water Pollution Control Administration except where it is judged that fire or safety hazards require the immediate application of such chemicals.

4. When chemical compounds are used in connection with oil clean-up, only those compounds exhibiting minimum toxicity toward the aquatic flora and fauna should be used. The Federal Water Pollution Control Administration is now developing and will soon issue a standard procedure for determining the toxicity of such chemicals.

5. Materials which aid in the collection of floating oils such as sorbents, gellants and viscosity control additives are considered to be generally acceptable providing that these materials do not in themselves or in combination with the oil increase the pollution hazard.

6. Research and development to improve chemicals which emulsify, disperse, solubilize or precipitate oil is encouraged. Whenever it is demonstrated to the complete satisfaction of the Federal Water Pollution Control Administration, that such a chemical, by itself and in combination with oil is non-toxic its use may be approved in the areas where the protection or preservation of (a) fresh water supply sources, or (b) major shellfish or fin fish nurseries, harvesting grounds or passage areas is a prime concern.

July 5, 1968

FLOATING SORBENTS

Absorbent (adsorbents) is a broad term defining in this report a type of material used in oil pollution control and clean-up. Most absorbents are described as oil-attracting (oleophilic) and water-repelling (hydrophobic). The use of absorbents involves placement in the oil slick, attraction of the oil to this material, and subsequent removal and disposal. Such materials include straw, hay, sawdust, rope, sisal, tree bark, peat moss, perlite, vermiculite, talc, pumice, various clays, seaweed, kelp, chrome leather wastes, rock wool sheets, glass wool, rayon floss, polymer beads and copolymers, polyurethane and polypropylene sheets, fibers and foam, rubber or latex, and cotton or textile wastes. Any of the above materials may also be specially treated in one or more ways to improve its absorbtive properties and handling characteristics. Furthermore, these materials may be used as integral part of oil recovery-pickup devices, booming systems, beach clean-up methods and other.

Absorbents are advantageous in that they generally do not add materials in solution and thereby contribute to the existing problem. They are also capable of picking up oils in large ratio to the amount of absorbent used. Major difficulties, particularly for large-scale spills, are in calculating and delivering sufficient absorbent in the proper form at the proper place and time, applying the materials over the water body, adequately collecting and transporting the oil-soaked mass to shore, in recovering oils and securing ultimate disposal of the mass. Fire hazard may also be increased

by use of many of these materials in confined places if ignition sources are present.

Many absorbents have performed quite well particularly in small-scale spills and may have high potential for moderate and even large-scale spills. Toxicity is far less a problem compared to dispersants since the absorbent material generally remains in solid state; however, certain absorbent products may need further evaluation in this respect. Comparison of the relative effectiveness between various products together with cost-considerations is presently lacking. This evaluation must be conducted both within the laboratory and under realistic field conditions. The FWPCA Research facility has initiated limited studies in this direction.

Straw is widely used as an oil absorbent because of ready availability, cheapness and accepted effectiveness. Straw is distributed manually or mechanically with or without shredding, and by any or all other means available at this time. Straw is most effective when used on shore or close to shore. Although straw can be effective in clean-up it must be adequately worked into the oil and its retrieval and disposal is a dirty, slow and tedious job, requiring equipment and considerable manual labor. In certain areas, soaked straw may not be burned because of air pollution codes and may not be buried in other areas because of potential groundwater pollution.

Far less use has been made of other absorbents compared to straw. Concerning natural absorbents, seaweed, kelp and indigenous grasses have been capable of absorbing appreciable oil in the TORREY CANYON, OCEAN EAGLE and

Santa Barbara incidents. Production of powdered pine bark has been initiated by a Swedish pulp and paper mill. It is reported that two pounds of bark will absorb about one gallon of oil with indicated costs around $5 per 33 pound bag of powdered bark. Preliminary data received from Sweden on peat moss show about two pounds of absorbent required per gallon of oil.

Natural products can be heated or chemically treated to provide modified materials for oil pollution control. Perlite, a naturally occurring volcanic rock receiving subsequent pulverization and thermal expansion, has received favorable reports in aiding oil recovery on San Juan beaches; however, its action was less certain in Santa Barbara and shown by FWPCA research studies conducted on New Jersey beaches in 1968. Cost is approximately $75.00 per 100 cubic feet absorbent. Vermiculite after treatment to render it expandable and hydrophobic has received mixed opinion in its ability to absorb oil. Certain vermiculite products are reported to rapidly absorb floating oils whereas others do not have the required affinity.

Absorbents derived from the synthetics or plastics manufacturing field represent an additional group of products with potential promise. These materials are generally high-molecular weight polymers or polyethylene, polystyrene, polypropylene and polyurethane. These agents may be applied as a light foam or plastic network by spraying, as a solid-state form in the form of pillows, sausage shapes, or otherwise shredded and distributed over the oil slick. It is reported in theoretical terms that polyurethane

foam can ultimately absorb over 90 percent of its own volume of oil or 100 times its own weight. Polypropylene is also reported as absorbing six times its weight in oil and one cubic yard capable of retaining 100 pounds of oil. These data represent extremely low cost required to clean up large volumes of oil but such figures likely reflect lab conditions which are far from those experienced in the field. Difficulties have been experienced with absorbing heavy and weathered oils. Effectiveness appears dependent upon prolonged time interaction, temperature, and other factors which must be better understood before many of the disappointments observed so far may be overcome.

It must also be noted no absorbent appears truly effective if left to its own resources. Agitation and increased interaction between the oil and the absorbent is highly desired whether induced by natural wind, wave or tidal energy forces or preferably by mechanical means. The problem of absorbent application becomes increasingly complex with the larger oil spills. In massive oil spills, the logistics required to acquire and properly apply sufficient amounts of absorbents and the consequent collection and disposal of the oily masses, become enormous.

SINKING AGENTS

Sinking agents are granular solids of high density and generally of fine structure. When applied over the surface of a slick, they adhere to the oil and there is subsequent absorption and ultimate sinking of the oil-mass. Typical oil-sinking agents include sand, brick dust, fly ash, slaked lime, stucco, cement, china dust, omya clay, volcanic ash, chalk, crushed stone, coal dust and specially-produced materials as carbonized-siliconized-waxed sands and fly ash.

Sinking agents are efficiently employed on the heavier or weathered oil slicks and when oil slicks are well-defined in thickness. Otherwise, quantities of materials required are rather prohibitive. It is doubtful that sinkants may be profitably used with thin films and light crudes. The absorbent must be evenly mixed with the slick and given proper time interaction before the ensuing mass eventually sinks. Furthermore, bonding of the agent with the oil must be nearly permanent and there should be little or no tendency for release of the entrapped and sunken oils back to the water environment.

The single known large-scale application of sinking agents was undertaken by the French during the TORREY CANYON. It is reported the French applied some 3,000 tons of calcium carbonate with about one percent of sodium stearate added to treat and sink about 20,000 tons of oil found in the Bay of Biscay and previously originating from the TORREY CANYON. Although good scientific data are generally lacking particularly as to amounts of oil

actually treated in this case, the oils were reported sunk in 60-70 fathoms and coastal pollution was minimized. The French success was attributed to good spreading and mixing of the chalk into the oil body, and high density of the weathered slick, thereby requiring considerably less absorbent as compared to fresher oils. Subsequent reports state that 14 months after the incident no sign of oil was found over the water surface. It must be noted on the basis of French experiences above, that oil-sinking agents have subsequently become more attractive and promising.

Opinions on the use of oil sinkants still remain divided as to efficiency, cost, application and detrimental environmental effects. Advantages of this type of treatment are:

1. Confinement of the oil pollution with its consequent damages into a fixed place on the sea bottom.
2. Minimum toxicity at least to the free-floating aquatic plants and animals.
3. Development of another means of fighting serious oil pollution spills.

Opposition to use of these agents has been generally ascribed to:

1. Smothering, destruction or contamination of sea bottom life.
2. Difficulty in properly transporting and applying large amounts of the agent(s) to the oil slick.
3. Possible resurfacing of the oil after some period of time.
4. Fouling of shellfish beds and fishing gear and equipment by the sinking oil-mass.

Economics of this treatment method varies widely because practically all data have been obtained from laboratory testing rather than from realistic field conditions. Early Department of Interior studies suggest three pounds of carbonized sand required to sink one pound of oil whereas other studies indicate ratios of one or less of sinker weight to oil weight depending upon density of oil slick and other factors. Large-scale application generally envisions spraying a slurry of sand or other mixture over the slick from a large vessel, hopper dredge, or equivalent. The cost of sinking agents is generally in the range of $20 to $80 per ton, depending upon quantity purchased, location and type of material required.

It appears the use of sinking agents would be most advantageous in deeper ocean waters outside the heavy-fishing zones. If resurfacing of the oils does occur, in this case, it should be gradual and far less objectionable in the event weathered oils were washed ashore at a later time.

GELLING AGENTS

The use of special gelling or congealing materials applied over the surface or periphery of an oil slick is another approach for containing and cleaning up oil spills. The gelling concept is also in the process of development for stabilizing liquid cargo aboard a stranded or heavily-damaged vessel at sea.

One patented product when applied in spray form, is reported to form a stiff gel with oil on water. When placed around the perimeter of an oil slick, the gel is said to form an effective chemical boom which prevents the oil from further spreading. The oil contained within the inner circle may be removed by mechanical means or the total slick may be gelled to facilitate removal. It is also claimed that the oils recovered in this manner may be profitably reclaimed. For example, the gelled mass may be mixed with fuel oil and burned as replacement bunker fuel.

Possible toxicity of this class of chemical is unknown but under current evaluation. Data from the manufacturer indicate approximately one part chemical is necessary per part of oil to be gelled, thereby giving an estimated cost of about $1.50 per gallon oil treated. However, these costs very likely reflect laboratory testing and assuredly would be on the low side for field application.

BURNING AGENTS

The concept of setting afire oils which have spilled and spread over the surface of a water body is potentially attractive principally because this approach offers an inexpensive means of disposing of the problem. Past attempts to burn oils upon the sea have been almost completely unsuccessful, especially the example of the TORREY CANYON. In the case of the TORREY CANYON, addition of thousands of gallons of aviation fuel, Napalm and sodium chlorate, together with aerial bombing of the vessel, failed to produce sustained burning. Spilled oil may possibly be burned by using catalytic or combustible agents or inducing "wicking" action between the oil and water.

In the "wick" theory, capillary action is induced in the oil slick and a portion of the oil is drawn up to the air (oxygen) interface to promote burning. Concurrently, the surface oil is partially insulated from the cooling effect of the sea water underneath. Wood, debris and flotsam emmeshed with the spilled oil apparently insulates this layer from the colder water body and sustains burning. Since freshly spilled crude oil contains a relatively high proportion of volatile components, its ignition is more feasible than weathered crude wherein much of the volatiles have already been lost. Besides potential materials as felting and asbestos-like agents, two commercial products are known which promote the burning of oils on water. One employs both a liquid and powder in controlled burning. The other is reported to consist of a specially-treated fine silica which

increases capillary action aiding in sustained and controlled burning. Neither product so far as known has been applied in large-scale, and therefore factors of logistics, application and amount of residue are unknown.

The problems of controlling the burning oil-mass, ensuing air pollution and disposal of residue would appear to preclude the use of this course of action except in those situations where the oil-mass is sufficiently distant from the shore face. In addition, the possible loss of the vessel or drill platform which may be the source of the spill, is another factor which must be recognized. Additional and refined procedures in burning are a consideration and because of the potential value of this method, further investigation should be carried out.